FUNCTIONAL PROPERTIES OF ELECTRICALLY CONDUCTIVE ADHESIVES AS INTERCONNECT MATERIALS

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A report submitted
In fulfilment of the requirement for the degree of
Bachelor of Mechanical Engineering (Hons)

Faculty of Mechanical Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2019

DECLARATION

I declare that this project entitled "The Functional Properties of Electrically Conductive Adhesive as Interconnect Material" is the result of my own work except as cited in the references.

Signature : ……………………………………..

Name : …………………………….…………

Date : …………………………….…………

APPROVAL

I hereby declare that I have read this project report and in my opinion this report is sufficient in term of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Hons).

Signature	:	....
Name of supervisor	:	....
Date	:	....

DEDICATION

This project work is dedicated to my beloved family for always been there to support and inspire me throughout my life.

ABSTRACT

The use of electrically conductive adhesive (ECA) been expanded widely in microelectronics industry. ECA is to replace solder with beneficial advantages in fastening and brazing, sealing, interconnection, electrical shielding and eco-friendly with elimination of lead usage and reduce flux cleaner, due to increasing awareness to the environment increased as the traditional solder no longer fulfil the increase of miniaturization of electronic device or product and contain toxic lead, harmful to human and hazardous material. This research is focused on the functional properties of electrically conductive adhesives as interconnect materials. In this research, hybrid electrically conductive adhesive was formulated by adding 5 wt.% silver flakes (Ag) and multi walled carbon nano-tubes (MWCNT) with filler loading 5 wt.%, 6 wt.% and 7 wt.% to the epoxy matrix in a centrifugal mixer, Thinky mixer ARE-310 machine. One of the objectives of this research is to establish a lower percolation threshold for electrically conductive adhesive with varying filler loading. The second objective is to investigate the effect of hybridizing the fillers on the mechanical performance of hybrid electrically conductive adhesives. With reference to ASTM F390 standard guideline, JANDEL model RM3000+, a 4-point probe was used to measure the resistivity of printed hybrid ECA, in which each sample was tested for 3 times to get reliable set of data. The mechanical performance is evaluated in term of the lap shear strength of the hybrid ECA as ASTM D1002. The experiment results from electrical characterization suggest that the sheet resistivity gradually reduced (an indication of increasing electric conductivity) from 5 wt.% up to 7 wt.% of the MWCNT which then plateaued, a possible indication of percolation threshold, that is associated with better conductive path between the Ag-MWCNT hybrids fillers in the hybrid ECA. Here, the sheet resistivity is stabilized at 0.45kW/sqr. However, in term of the lap shear strength there is a decrease in the value with increasing MWCNT filler loading, from 8.61 MPa down to 7.03 MPa. At 5 wt.% the hybrid ECA exhibit a combination of cohesive-adhesive failure, in which the hybrid ECA is retained at both sides. However, at 7wt% MWCNT, the hybrid ECA experience an adhesive failure since the hybrid ECA is retained only on one side.

ABSTRAK

Penggunaan "electrically conductive adhesive" (ECA) telah berkembang secara meluas dalam industri mikroelektronik. ECA adalah untuk menggantikan pateri berasaskan plumbum dengan kelebihan dalam pengikat pateri, penyegal, interkoneksi, perisai elektrik dan mesra alam dengan penghapusan kegunaan plumbum dan mengurangkan kegunaan plumbum dan mengurangkan pembersih fluks, kerana peningkatan kesedaran kepada pateri plumbum tidak lagi memenuhi peningkatan daripada pengecilan peranti electronik atau produk dan mengandungi bahan plumbum toksik, boleh membahayakan kesihatan manusia. Penyelidikan ini memberi tumpuan kepada sifat-sifat fungsional "electrically conductive adhesive" sebagai bahan sambung. Dalam penyelidikan ini, hibrid ECA telah diformulasikan dengan menambah 5 wt.% serpihan perak (Ag) dan "multi-walled carbon nano-tube" (MWCNT) dengan kandungan 5 wt.%, 6 wt.% and 7 wt.% matriks epoksi dalam pembancuh sentrifugal, mesin "Thinky ARE-310". Salah satu objektif penyelidikan ini adalah untuk mewujudkan "percolation threshold" yang rendah untuk hibrid ECA. Tujuan kedua adalah untuk mengkaji kesan hibridsasi pengisi prestasi mekanikal pada hibrid ECA. Dengan merujuk kepada garis panduan standard ASTM F390, model JANDEL RM3000+, "4-point probe digunakan untuk mengukur sesitiviti hibrid ECA, setiap sampel diuji selama 3 kali untuk mendapatkan set data yang lebih tepat. Prestasi mekanikal dinilai dari segi "lap shear strength" untuk hibrid ECA sebagi ASTM D1002. Eksperimen yang dihasilkan dari pencirian elektrik menunjukkan bahawa "sheet resistance" berkurang secara beransur-ansur (indikasi peningkatkan kekonduksian elektrik) dari 5 wt.% sehingga 7 wt.% kemudian mendatar, menunjukkan kemungkinan "percolation threshold", ia mengaitkan laluan konduktif yang lebih baik antara kandungan Ag-MWCNT hibrid. Di sini, "sheet resistivity" stabil pada 0.45 KW/sqr. Walau bagaimanapun, dari segi "lap shear strength" terdapat penurunan nilai dengan peningkatan kandungan MWCNT, dari 8.61 MPa hingga 7.03 MPa. Pada 5 wt.%, hibrid ECA mempamerkan gabungan "cohesive-adheisve", di mana hibrid ECA mengalami dikekalkan di kedua-dua belah permukaan. Walau bagaimanapun, pada 7 wt.% hibrid MWCNT mengalami kegagalan "adhesive" kerana kebanyakannya melekat di belah permukaan.

ACKNOWLEDGEMENT

A special gratitude and thanks also to all the parties involves either directly or indirectly. With the cooperation of all parties, I have been able to complete this final project. Firstly, a special thanks to my final year project supervisor, Dr. Siti Hajar Binti Sheikh Md. Fadzullah, who offers me countless valuable knowledge, stimulating suggestion, coordinating and encourage me to fill up my project completely especially in writing this report.

I would also like to acknowledge with much appreciation to the all the technician and lecture in Mechanical Engineering Faculty, who gave the permission to use all the required machinery and the necessary material to complete the project. Especially thanks to Muhammad Muaz Bin Nasarudin, an MSc student from the Faculty of Mechanical Engineering for his advice, time, and willing to share knowledge with me throughout the experiment. Secondly, I would also like to thanks to my dearest family members who gave given us full support of encouragement and helps us in terms of financial.

Last but not least, I would like to express my gratitude towards the panels. Without their gratitude, comment, improvising of ideas and tips I will never know my mistake and also cannot improves weakness especially in my project presentation. And I also like to make an appreciation to my friends who help me a lot in finishing this project success. Hopefully this research will bring benefit and guidance to other students and researches.

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURE

LIST OF ABBREVIATIONS

Ag	Silver
ASTM	American Society For Testing Material
CB	Carbon Black
CNT	Carbon Nano-Tube
DWCNT	Double-Walled Carbon Nano-Tube
ECA	Electrically Conductive Adhesive
FED	Flat Emission Display
ICA	Isotropic Conductive Adhesive
LCD	Liquid Crystal Display
MWCNT	Multi-Walled Carbon Nano-Tube
SWCNT	Single-Walled Nano-Tube

LIST OF SYMBOL

ω-cm	electrical resistivity
cm	Centimetre
°c	Degree Celsius
G/cm3	Density
GPa	Giga Pascal
Mpa	Mega Pascal
Pa	Pascal
G	correction factor
k	Kelvin
Ω	Ohm
sq	Square
wm−1k−1	Thermal conductivity
sm−1	conductivity
λ	Lambda
L	Length
meq/g	milliequivalents
mm Hg/oC	Vapor pressure
pt-co	Platinum-Cobalt Scale
nm	Nanometer
µm	Micrometer
V	Voltage
I	Current
Ω/sq	sheet resistance
t	thickness
UTM	Universal Testing Machine
rpm	Revolutions per minute

CHAPTER 1

INTRODUCTION

1.1 Background

The use of electrically conductive adhesive (ECA) been expanded widely in microelectronics industry. The main application for the electrically conductive adhesive (ECA) is die attachment, surface mounted assembly of package component on wiring printed board, liquid crystal display (LCD). The use of electrically conductive adhesive (ECA) is to replace solder with beneficial advantages in fastening and brazing, sealing, interconnection, and electrical shielding do come with friendliness advance as elimination of lead usage and reduce flux cleaner (Drive, 2010). Compared to other types of adhesives, electrically conductive adhesive (ECA) function as electrical interconnection between two bonded surface and join with sufficient strength on bonded surface. The electrically conductive adhesive (ECA) composed of composites in the form of dispersion of particle in an insulating adhesive matrix. Carbon black, micron or Nano-sized particle silver, gold, and aluminium, and graphite flakes are the common filler used as conductive filler and as for the polymer matrices, epoxy, silicone, polyurethane, and polyamide are the common materials employed. These adhesives have high and stable electrical conductivity, and normally the electrical resistivity of 10^4 Ω-cm, which is higher than metallic conductors. From the literature, past study have investigated a mixture of metal filler into epoxy resin to improve its functional properties such as thermal conductivity, strength and the composite coefficient of thermal expansion (CTE), shrinkage, and heat resistance (Sancaktar and Bai, 2011).

Isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA) are two main classification of electrically conductive adhesive (ECA) (Yi Li Daniel Lu C.P. Wong, 2010). Isotropic conductive adhesive (ICAs) can be either thermoset or thermoplastic. Thermoplastic has long curing time but rework-able. Meanwhile, thermoset form chemical cross link between polymer chains when undergoes chemical reaction and has poor rework ability and limited shelf life. Anisotropic electrical conductivity (ACAs) normally purpose for substitution of lead-free solder when undergo assembly expose with high heat sensitive component, which will cause damaged under temperature applied soldering process. The ICAs commonly used for fine-pitch assembly, it advance in low frequency and no bridging in adhesive compared to lead solder (Republic, 2011). Carbon Nanotube (CNT) features unique characteristic; it has good chemical stability, conduct electricity, and exhibit strong mechanical properties. Carbon Nanotube (CNT) are divided into two types; single walled carbon Nanotube (SWCNT) and multi walled carbon Nano-tube (MWCNT). Single walled carbon Nanotube (SWCNT) has one dimensional structure and relatively more expensive to produce. Multi-walled carbon Nano-tube (MWCNT) consists of multi-layer of graphite roll in one tubes, and unique in mechanical and electrical properties will be new application in material and devices(Mantena, 2009).

1.2 Problem Statement

With an increasing concern and better awareness to protect the environment, therefore, it is no more favourable to consider traditional solder which contain toxic lead, since it is harmful and hazardous material to human health (luo *et al.*, 2016). Due to lead-solder low resolution, it has no longer fulfil the demand for increase in miniaturization of electronic device or product (Zhang *et al.*, 2011). To replace the lead-based solder, lead free electrically conductive adhesive (ECA) is develop, which comes along with many advantages such as low temperature processing, simple processing and finer pitch. However, some of the major drawbacks of the electrically conductive adhesive (ECA) in comparison to the lead-based solder include low mechanical strength, limited impact resistance, and high or increase in contact resistance increased, hence inferior electrical conductivity (Mantena, 2009).

Carbon Nano-tubes (CNT) is introduced to replace the lead based solder. It exhibits unique characteristics in terms of mechanical, electrical, structure, and thermal properties. With the advantages in easy preparation, less amount of limitation in size, it is used to fabricate CNT firm (Pan, Zhu and Gao, 2008). CNT is the stiffest and strongest fibre among others with unique characteristics; stable in chemical, strong and conductive electricity (Mantena, 2009).

In this research project, epoxy is mixed with two conductive fillers: these being Multi-Walled Carbon Nano-tube (MWCNT) which is hybridize with silver flakes to formulate with varying filler loading of the MWCNT.

1.3 Objective

The objectives of this research project are:

I. To determine the percolation level for the electrically conductive adhesive with varying filler loading and two types of filler

II. To investigate the effect of varying the filler loading and types on the lap shear strength of the electrically conductive adhesives.

1.4 Scope of Project

The scope of this research projects is listed as below:

I. Formulation and fabrication of electrically conductive adhesives.

II. ECA sheet resistance measurement by conducting a four-point probe test on printed ECA.

III. ECA mechanical testing via lap shear test.

IV. Morphological study on substrate surface and fractured surface of the ECA.

1.5 Planning and Execution

The research activities for PSM I and II are shown in Table 1.1 and 1.2 respectively. The research activities include project tittle selection, literature review, experimental design, formulation and fabrication of ECA, ECA sheet resistance measurement and lap shear test on ECA as well as the failure analysis of the hybrid ECA using visual observation. For both semester, the completion of all research activities is followed by data analysis, report writing, report submission and the presentation during the seminar for each semester.

Table 1.1: Gantt chart for PSM 1.

WEEK / ACTIVITIES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Research title selection																
Literature review																
Experimental design																
Formulation and fabrication of ECA																
ECA electrical conductivity test																
Preliminary data analysis																
Report writing																
Report submission																
PSM 1 seminar																

Table 1.2: Gantt chart for PSM II.

WEEK / ACTIVITIES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Literature Review																	
Methodology																	
Conduct Experiment: Electrical Conductivity																	
Conduct Experiment: Lap Shear Test																	
Data Analysis																	
Progress Report Submission																	
Report Writing																	
Draft Submission																	
PSM II Seminar																	
Report Submission																	

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a review on the electrically conductive adhesive (ECA) which include the type of polymer matrix, type of filler, type of carbon nanotube, and functional properties ECA which is reported in the literature.

2.2 Electrically Conductive Adhesive (ECA)

The production of the solar cell is now doe by the leaded soldering. Electrically conductive adhesive to replace the standard soldering, as lead free and provides a gentle interconnection (Eitner *et al.*, 2012). The electrically conductive adhesive is found out have more application owing to numerous advantage such as the ability to bond two irregularly shaped surface, corrosion resistance, and proficient mechanical load transfer, stress and mechanical vibration resistance. These adhesive can be applied onto the film, adhesive joint and coating. Electrically conductive adhesive is a type of composite adhesive that comprised of two materials, the polymer binder resin (form of thermoset like: epoxy), conductive filler material (silver, gold, aluminium). This composite materials is an alternative electronic packaging material to the lead based solder, have advantage in high shear strength, environment friendly, save time(reduce in process step compared to solder), low temperature process, and accurate pitch capabilities (Trinidad *et al.*, 2017).

The used of electrically conductive adhesive (ECA) is shown to be an effort in replacing the soldering interconnection with an alternative substitute material such as the ECA.

Electrically conductive adhesive is a polymer composite system containing conductive particles and engineered to produce chemical and electrical bonds upon treatment and application. The treatment is normally heated up about in range of 120 °C to 180 °C. The electrically conductive adhesive can be used as a paste by dispensing or screen printing, conductive firm/tacky material, and pre-cured. The bonding process used in conductive adhesive and film does in principle not required larger areas as soldering(Beaucarne *et al.*, 2015). A schematic diagram of an electrically conductive adhesive bonded to an electrical component and connecting pad (Trinidad, 2016) is shown in Figure 2.1.

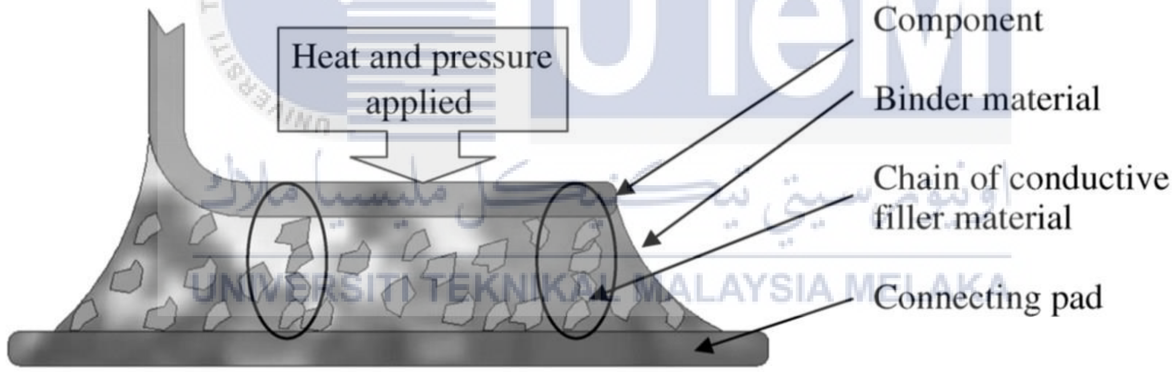


Figure 2.1: Schematic example of an electrically conductive adhesive bonded to an electrical component and connecting pad (Trinidad, 2016).

2.2.1 Polymer Matric Composite.

Polymer matric composites used organic polymer as matrix and fibre as reinforcement. Fibre have its own strength and modulus that higher compared to matrix material. Thus, main load bearing component were fibre. That is why matrix material must have good adhesive properties to firmly bond fibre together, to transfer applied load to the fibre, and serve to uniformly distribute the applied load. In composites materials, the interface between the fibre and matrix interface deflect their performance. Polymer matrix composites have their inherent characteristics, and become the fastest growing and most widely used composites. Table 2.1: shows that these materials high specific strength and modulus, specific strength is the ratio of density and strength, the high specific modulus is ratio of modulus and density.

Table 2.1: Specific strength and specific modulus of some common used materials and fibre composites (Ru-Min Wang, 2011).

Materials	Density (G/cm^3)	Tensile Strength (GPa)	Elastic Modulus (10^2GPa)	Specific Strength (10^6Cm)	Specific Modulus (10^8Cm)
Steel	7.8	1.03	2.1	1.3	2.7
Aluminium alloy	28	0.47	0.75	1.7	2.6
Titanium alloy	4.5	0.96	1.14	2.1	2.5
Glass fibre composite materials	2.0	1.06	0.4	5.3	2.0
Carbon fibre ii/epoxy composite materials	1.45	1.50	1.4	10.3	9.7
Carbon fibre i/epoxy composite materials	1.6	1.07	2.4	6.7	15.0
Organic fibre/epoxy composites	1.4	1.40	0.8	1.0	5.7
Boron fibre/epoxy composites	2.1	1.38	2.1	6.6	10.0
Boron fibre/aluminium matrix composites	2.65	1.0	2.0	3.8	7.5

Crack propagation can be prevented at the interface of fibre and matrix in composites materials. Composite material will not easy lose the bearing capacity in short term, or fracture and crack in sudden development. The disadvantage of polymer matrix composite can harm human during its process, by emitted more hazardous substance during material process, dangerous toxic and worse material manufacturability. Material do has advance in applicability and economics but harm to human, have limit is usage and development(Ru-Min Wang, 2011).

2.2.1.1 Thermoplastic

Thermoplastic is one of the world widely recognizable real-world application of chemistry is the development of plastic. Thermoplastic is also know well as recyclability and versatility (Mayer and April, 2018). Thermoplastic can be melted, cured and forth, but there is limit of time in process repeating process depend on the particulars of the materials, thermoplastic is capability in melted multiple times without degrading the material (Efficiency, 2018). Thermoplastic have large scale range in properties. They can be much as rubber, and at the same time strong as aluminium. The weight of the thermoplastic with densities of 0.9 to 2 gm/cc, and can withstand extremes temperature up to 600 °f or 315.56°c. They are excellent insulator material in electrical and thermal. Electrically conductive with the addition of the carbon or metal fibre is made up of thermoplastic composites. Thermoplastic can be produce in very high volume with high precision with low cost, proper range of properties, energy efficient in manufacture and processing (Fax, 2018). An example of a thermoplastic resin structure (Liu, Zwingmann and Schlaich, 2015) as shown in Figure 2.2.

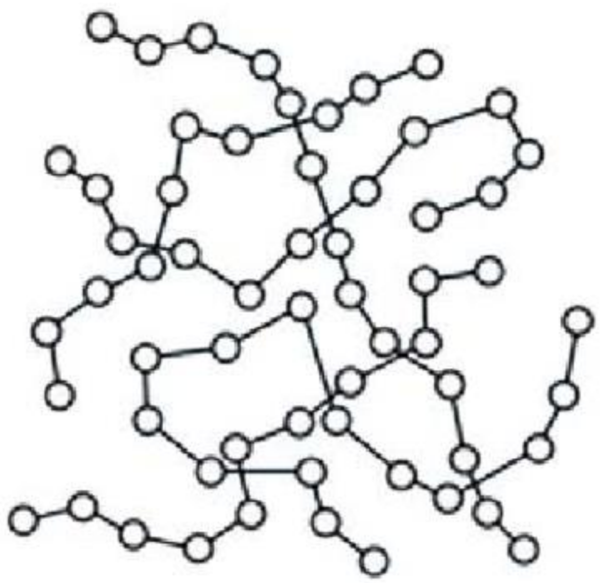


Figure2.2: Thermoplastic chemical structure (Liu, Zwingmann and Schlaich, 2015).

2.2.1.2 Thermoset Plastic

Thermoset materials can be melted for only once. It cannot been remolded, otherwise will burn out during the process rather than melt (Efficiency, 2018). Thermoset is a synthetic material, when heated it will gain the strength but cannot be remoulded or reheated after first heat deforming. Thermoset polymer is good in corrosion, chemical resistance, high melting point, shrink properties and exhibit low creep. Thermoset polymer is used in a variety of application and end-market due to its excellent heat and corrosion resistance properties. Thermoset consist good dimension and stability in chemistry during expose to heat and high operating temperature that make engineer and designer interest to implement. Thermoplastic monomer has two reactive end for liner chain growth. Meanwhile, the thermoset monomer have more than two reactive end, molecular chains crosslinking in 3-D. All the molecules interconnected with permanent, strong, physical bond, and not heat reversible

(Adhesiveandglue, 2018). An example of a thermosetting resin structure (Liu, Zwingmann and Schlaich, 2015) as shown in Figure 2.3.

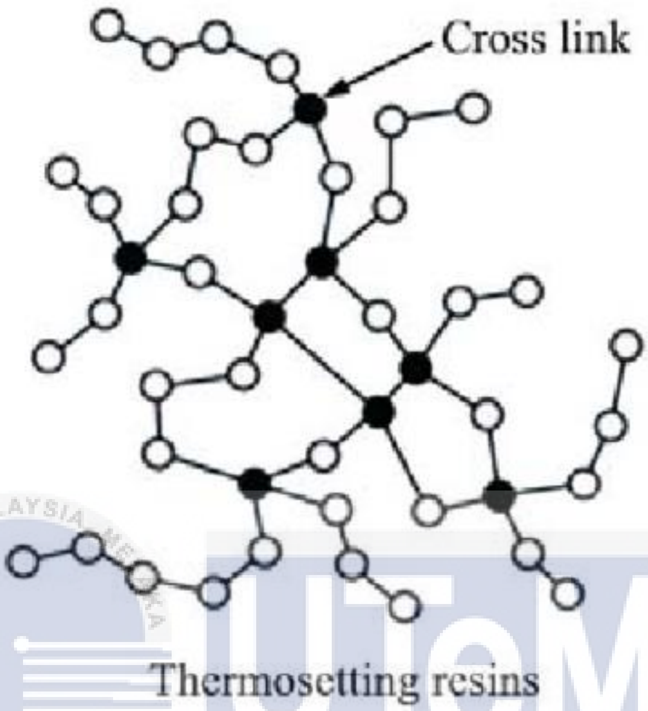


Figure2.3: Thermoset chemical structure (Liu, Zwingmann and Schlaich, 2015).

2.2.1.2.1 Epoxy

Epoxy is widely used as electrically conductive adhesive (ECA), with high tensile strength and modulus, low shrinkage in cure, corrosion resistance, good chemical, high adhesive and stability dimensions (Kwon *et al.*, 2011). Epoxy concrete and mortar offer many engineering application, like flooring, abrasion, pavement, precast products, chemical resistant, adhesive properties, repair owning to their superior and anticorrosive linings. Precautions must be taken when handing epoxies since they are hazardous to human health. Some of the common hardeners of epoxy resin were amine type; aromatic, cycloaliphatic, and aromatic. The amount, type, functionality of the hardener, as well as the curing conditions (curing time & temperature) influence properties of hardener epoxy resins (Ozeren Ozgul and Ozkul, 2018).

2.2.2 Filler for ECA Composite

Filler or conductive filler are materials in the form of powder, fibre, and materials that will mixed be with epoxy to function as conductive for easier the electricity/electron transfer. Conductive filler available in variety of material like; metal, non-metal, metallic, and metallic oxide coating. They are used in many applications, depending on the conductivity, high conductive filler used in electrodes, electrical contact materials, and conductive wiring, since it have low resistance. With the high resistance, it is used in electrical heating wires or heating elements to prevent from static electricity electrification (Kim *et al.*, 2004).

2.2.2.1 Metal

Metal has highly electrical and thermal conductivity, ductility and high reflectivity of light. Metals are found in ores (mineral-bearing substances) like copper, gold and silver they not react with other element. Atoms of metal have less than half the full complement of electron in outermost shell so they tend not to form compound with each other. Less reactive metals are silver, gold and platinum but high reactive metals include lithium, potassium and radium. The mechanical properties of metal is the ability to resist, hardness, fatigue strength, ductility and malleability (BELL, 2019).

2.2.2.1.1 Silver (Ag)

Silver (Ag) is the most popular among other metal as electrically conductive filler in electrically conductive adhesive ECA due to it high electrical conductivity. Nonetheless, some of the main disadvantages of silver when blended with epoxy include low electrical and thermal conductivity, poor impact strength, and limited current carrying capability (Qiao *et al.*, 2014). Moreover, although silver has high conductivity but come with high cost, nonetheless their contact resistance increase dramatically at elevated temperature or humidity ageing (Wu *et al.*, 2007).

2.2.2.A.1 Silver Flakes (Ag)

Silver flakes has thin layer surface of organic lubricant and used as filler in electrically conductive adhesive (ECA). The layer of lubrication on the silver flakes surface needed for eliminating the silver particle agglomeration while dispersing the silver filler into the polymer resin. Silver flakes has highest electrically conductive compared to the others metals, silver flakes were produced from silver powder using mechanical milling. Organic lubrication is added during the milling process to form a thin layer on the surface after product it. The thin layer of lubrication is nonconductive. Once the thin layer is removed, the electrically conductive adhesive (ECA) will then become conductive(Lu, Tong and Wong, 1999).

2.2.2.A.2 Carbon Black (CB)

Carbon black (CB) is can be widely found in several products. Plastic, vehicle tyre, toners, printing ink, electrostatic discharge and more. Carbon black have more than 97% of carbon in grape-like cluster aggregates, smallest invisible of carbon black unit with various sizes, surface chemistry, specific surface area and microstructure. Carbon black used in polymer composite purpose of electromagnetic interference shielding, conductive adhesive, electrostatic discharge shields for sensing applications also the conductive photoresists as electrically conductive micro-components (Hauptman *et al.*, 2012). Carbon black with volume resistivity about 0.1 to 10ω.cm as semiconductor material. Raw material of carbon back is easier to locate and the conductive properties very last longer and stable. Sensor component is normal made up carbon black due greatly adjust the resistivity of composite material (Liu, Zheng and Liu, 2018). Carbon black not only easy to found but it also low cost and possesses high conductivity values

($\rho \sim 10^{-5}$ ω m) good in polymer and epoxy based composition thick coating layer (enríquez *et al.*, 2014). Carbon black been used for decade as conductive filler added into polymer based composite (hou, zhou and wang, 2018).

2.2.2.2 Non- Metal Fillers

Non-metal are not capable to conduct electricity or heat. Non-metal are very brittle and not able to roll into wires or pounded into sheet. They can be categorized in two of the three state of matter; gases (i.e. oxygen), solid (i.e. carbon) (Bentor, 2018). Atoms of non-metal were generally small and contain relatively large number of electron in outermost shell, nearly filled electron shells, hence needed some additional electron to be balance. It has pronounced tendencies to attract electron to themselves due to other electron were low electronegativity (Physician *et al.*, 2017).

2.2.2.2.1 Carbon Nano-Tube (CNT)

Carbon Nano-Tube (CNT) have attracted a lot of attention as a potential cathode material and used in flat emission display (FED) with its own unique structure, electrical, mechanical, and thermal properties. Carbon Nano-Tube have been adopted in fabrication using screen printing technology because it is low cost, small limitation size, and easy to prepare (Pan, Zhu and Gao, 2008). Carbon Nano-Tube (CNT) films depend on their purity, tube, lighting, bolometric detector, display device, quality, diameter, good potential on market transparent electronic, and electrode for solar cells (Iakovlev *et al.*, 2018). Carbon Nano-Tube (CNT) properly with come the next generation of high electrical conductive due to it benefits of high mechanical performance, light weight, high thermal conductivity and low cost. With unique of physical and electrical properties, it able to reduce percolation thresholds in matrix and intrinsic electrical resistivity. Next, Carbon Nano-Tubes has highly aspect ratio, can be optimal materials for connecting metal flakes in electrically conductive adhesive (ECA) for constructing conductive network and reducing metal content, thus minimizing the cost of electrically conductive adhesive. Carbon Nano-Tube (CNT) will be the one of the most promising filler for low cost electrically conductive adhesive (ECA) (Luo *et al.*, 2016). Carbon Nano-Tube (CNT) were categorized into Single-Walled Carbon Nano-Tubes (SWCNT) and Multi-Walled Carbon Nano-Tubes (MWCNT) (Hirsch, 2002).

2.2.2.2.1.1 Single-Walled Carbon Nano-Tubes (SWCNT)

Single-Walled Carbon Nano-Tubes (SWCNT) do meet the material characterises; low resistance, light weight, low cost, easy prepare, and high transmittance. It very suitable for passive photonic devices, lighting, display devices, electrode for solar cells, bolometric detector, good potential on market of transparent electronic. The characteristic of Single-Walled Carbon Nano-Tubes (SWCNT) is depend on the bundle, orientation of tube and size (iakovlev *et al.*, 2018).

2.2.2.2.1.2 Multi-Walled Carbon Nano-Tubes (MWCNT)

Multi-Walled Carbon Nano-Tubes (MWCNT) is similar in certain aspect with single-Walled Carbon Nano-Tubes (SWCNT) but have differences striking. MWCNT have several tubes in concentric cylinder show in Figure 2.4. The number of concentric wall may vary from 6 to 25 or more. The diameter of MWCNT is 30nm, as compared to SWCNT, which is only in range between only 0.7-2.0nm.

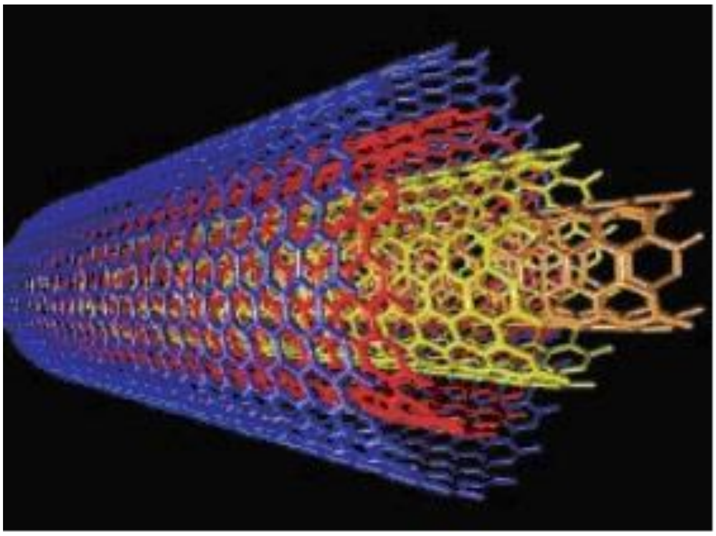


Figure 2.4: Multi-Walled Carbon Nano-Tubes.

MWCNT has great properties such as highly conductive once it properly integrated into composite structure. High chemical stability and aspect ratio with length more than 100 times the diameter, do higher in certain cases, stability thermal more than 600 °c, depend on defect level once intergraded into composite. MWCNT is suitable for uses in electrically conductive polymer composites because it has very high conductive and aspect ratio. Electrostatic discharge protection in wafer processing fabrication, RFI shielding materials, plastic component for automobile fuel line components, and plastic rendered conductive to enable electrostatic, those application evolved MWCNT (AZoNano, 2013).

2.3 Functional Properties of ECA Composites

Properties of ECA can be individualize in two to categorize: electrical and mechanical properties.

2.3.1 Electrical Properties of Electrically Conductive Adhesive (ECA).

The function of electrically conductive adhesive (ECA) is to form electrical connection with desired electrical conductivity between different electronic part to form circuit. Four point probe four terminal sensing or know as kelvin (chandra *et al.*, 2017) sensing is named after William Thomson, Lord Kelvin, a person who invented it, which can measure the wire resistance, showed very low resistivity, and eliminate inaccuracy (Amoli, 2015). A four point probe was used to measure the electrical sheet resistance of electrically conductive adhesive (ECA) (Trinidad, 2016).

2.3.2 Mechanical Properties of Electrically Conductive Adhesive (ECA).

Mechanical properties of conducting composite in electrically conductive adhesive are important for many application in electronic assemblies and component (ma *et al.*, 2009). For adhesive strength. as an example, the lap shear testing is used to determine the adhesive strength of metal to metal joint (Trinidad, 2016). The testing standard from the American society for testing material (ASTM) is one of the main reference for testing and evaluation of adhesive lap shear strength. Hence, the adhesive is utilized to form bond or joint between adherent materials which can be metal, wood, or plastic to identify adhesive bond or joint mechanical properties such as strength, creep, fatigue, and fracture (American society for testing materials, 2018).

2.4 Hybrid Electrically Conductive Adhesive

More recently, there is increasing attention of the development of hybrid filler for electrically conductive adhesive (ECA). From the literature, the function performance of the hybrid ECA is reported based on their type, size and shape of the filler. As an example, it was argued that, in order to establish better performance of thermal conductivity for ECA, an appropriate conductive filler mixing with matrix resin is required (Qiao *et al.*, 2014).

Mixing the conductive of micro and Nano filler is relatively a new method to improve the electrical conductivity of the hybrid ECA. New type of hybrid ECA is mixture of carbon nanotube (DWCNT or MWCNT) with silver flakes. The CNT and silver flakes has low percolation threshold in epoxy matrix and intrinsic electrical, remain stable conductivities compared to metallic Nano micro-particles, and low thermal conductivity. From the literature, it was reported that hybrid ECA with combination of silver flakes and CNT results in very high electrical and thermal conductivity, in which the individual conductivity of silver flakes, is reported as $6x10^7\ sm^{-1}$, while the CNT exhibit a value in the range of $1x10^4$ to $2x10^5 sm^{-1}$. With high aspect ratio and electrical conductivity of CNT, it is possible to reduce the amount of silver required compared to single conductive filler system such as the Ag filled adhesives (Marcq *et al.*, 2011).

CHAPTER 3

METHODOLOGY

3.1 Overview of Research

This chapter present the Hybrid ECA method of fabrication, types of testing, substrate and failure analysis of the hybrid ECA. Information about the raw materials, specific materials formulation and sample preparation is also included in this chapter. The methodology summarized for this research is shown in Figure 3.1, in which the flowchart provides an overview of all the experimental works involved for this project.

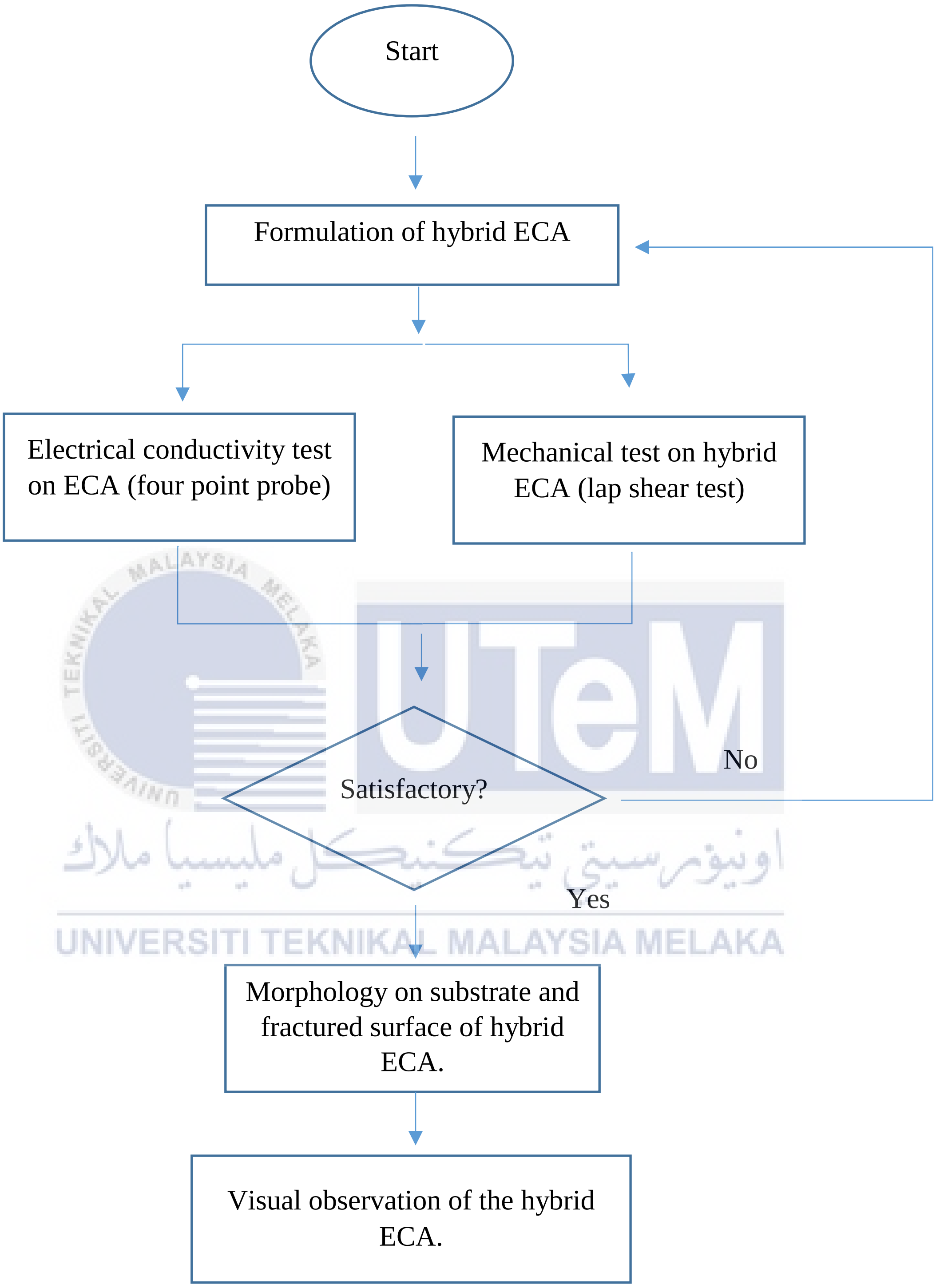


Figure 3.1: Flowchart of the experiment work involved in this project.

3.2 Raw Materials

3.2.1 Polymer

Epoxy has high tensile strength and modulus, corrosion resistance, good chemical, high adhesive and stability dimension, low shrinkage in cure (Kwon, Yim, Kim, & Kim, 2011). Araldite 506 epoxy resin is selected for this ECA polymer matrix. Epoxy is supplied by Sigma – Aldrich. Precautions must be taken when handling epoxy since this material have hazardous, therefore requires the use of appropriate clothing and protection. Table 3.1a shows the GHS classification and Table 3.1b shows material chemical and physical property.

Table 3.1a: GHS classification in accordance with 29 CFR 1910 (OSHA HCS)(Anonymous, 2017).

Type of hazard	Category	Warning
Skin irritation	2	H315- Causes skin irritation.
Eye irritation	2A	H319- Causes serious eye irritation
Skin sensitisation	1	H317- May cause an allergic skin reaction.
Acute aquatic toxicity	2	H401- Toxic to aquatic life.
Chronic aquatic toxicity	2	H411- Toxic to aquatic life with long lasting effects.

Table 3.1b: Chemical and physical properties of araldite 506 epoxy resin(Anonymous, 2017).

Appearance	From: semi-solid melting to liquid Colour: colourless
Melting and freezing point	-15°C & -5 °C
Flash point	252 °C
Vapour pressure	0.04 hPa (0.03mmHg) AT 77 °C
Relative density	1.168 g/cm 3
Partition coefficient –octano/water	Long Pow: 2.8

3.2.2 Hardener

Polyether amine D230 also called as JEFFAMINE D-230 Polyether amine supplied by Huntsman Singapore Pte LTD is used in fabrication of ECA, it has colourless to yellow liquid and the average of molecular weight is around 230 come with low viscosity, low chroma, and low vapour pressure. Application of hardener act as adhesive curing agent. Table 3.2a shows the material specification and Table 3.2b shows the material properties.

Table 3.2a: Specification of polyether amine D23 (Garibay-Vasquez, 2005).

Item	Standard data	Typical testing result
Appearance	Colourless to light yellow transparent liquid	Colourless to light yellow transparent liquid
Colour, apha	60 max	10
Water (%)	0.50 max	0.26
Total amine (mmol/g)	7.40 min	7.83
Primary amine content (%)	90 min	94.90

Table 3.2b: Properties of polyether amine D230(Garibay-Vasquez, 2005).

Properties	Polyether Amine D230
Colour, pt-co	30
Brookfield viscosity, cps, 25°c	9
Specific gravity, 20/20°C	0.948
Density , lb/gal, 20°C	79
Refractive index,n^{20}	1.4466
Flash point, PMCC, °C	121
Water, wt. %	0.1
Total acetylatables, meq/g	8.7
Total amine, meq/g	8.4
Primary amine, meq/g	8.2
Vapor Pressure, mm Hg/oC	1/101
Equivalent weight with epoxies ("amine hydrogen equivalent weight," or AHEW)	60
pKa	9.46
Appearance	Colourless to slight yellow with slight haze
Color, pt-co	60 max.
Primary amine, %	97 min.
Total amine, meq/g	8.1 min. 8.7 max.
Water, %	0.25 max

3.2.3 Multi-Walled Carbon Nano-Tubes

The Multi-Walled Carbon Nano-Tubes is supplied by nanostructured & amorphous material Inc. (NanoAmor), USA. It has high conductive when integrated into composite structure. High chemical stability and aspect ratio with length more than 100 times the diameter. When handle this material should be more take precaution do wear eye, hand protection it is hazardous chemical. Table 3.3a shows the material chemical and physical properties, and Table 3.3b shows MWCNT specification.

Table 3.3a: Chemical and physical properties of Multi-Walled Carbon Nano-Tube (Anonymous, 2011).

Form	Powders
Colour	Black
Odour	Odourless
Melting point	3652-3697 °C
Density	At 20 °C~ 2.1g/cm^3
Water	Insoluble

Table 3.3b: MWCNT specification (Anonymous, 2018).

Purity	>95 wt.% (carbon nanotubes)
Outside diameter	10-20 nm
Inside diameter	5-10 nm
Length	10-30 μm
SSA	> 200m^2/g
Ash	< 1.5wt%
Electrical conductivity	> 100 s/cm
Tap density	0.22 g/cm^3
True density	~ 2.1 g/cm^3

3.2.4 Silver Flakes, Ag

Silver flakes (Ag) been applied as filler for electrically conductive adhesive (ECA) for decades(Tech and Tong, 2013). Supplied by sigma – Aldrich. Silver come in form of flakes, with 1.59 μΩ-cm, 20°C resistivity and particle size 10 μm. Table 3.4a shows the classification of the hazardous chemical according to CLASS regulations 2013 and Table 3.4b shows the physical and chemical properties.

Table 3.4a: Classification of the hazardous chemical according to CLASS regulations 2013 (Anonymous, 2019).

Type of hazard	Category	Warning
Acute hazard	1	Hazardous to the aquatic environment
Chronic hazard	1	Hazardous to the aquatic environment
H410	-	Very toxic to aquatic life with long lasting effects.
P273	Prevention	Avoid release to the environment.
P391	Response	Collect spillage.
P501	-	Dispose of contents/ container to an approved waste disposal plant.

Table 3.4b: Physical and chemical properties (Anonymous, 2019).

Appearance	Form: flakes
Melting point/freezing point	Melting point/range: 960 °C - lit.
Initial boiling point and boiling range	2.212 °C - lit.
Relative density	10,49 g/cm3
True density	~ 2.1 g/cm^3

3.3 Electrically Conductive Adhesive (ECA) Preparation

For the hybrid electrically conductive adhesive is prepared consisting of the following materials:

Matrix		Filler loading 1		Filler loading 2
Epoxy	+	Multi-Walled Carbon Nano-Tubes (MWCNT)	+	Silver flakes

The amount of materials was added according to the weight percentage (wt.%), using the Rule of Mixture using equations (3.1) and (3.2):

$$W_{fraction} = \frac{W_{filler}}{W_{composite}} \tag{3.1}$$

$$W_{composite} - W_{filler} = W_{matrix} \tag{3.2}$$

The $W_{fraction}$ is the MWCNT and silver flakes weight fraction which used in this PSM I and PSM II were 5wt.%, 6wt.%, 7wt.%. $W_{composite}$ Total mass of composite which is 5 gram. W_{filler} is the mass of MWCNT required and W_{matrix}, mass of polymer matrix. For hardener, multiply 30% from W_{matrix} to determine the mass. Using the expression given in equation (3.3) below:

$$W_{matrix} \text{ X } 30\% = \text{weight of hardener in gram} \tag{3.3}$$

Table 3.5: Formulation of hybrid ECA.

Silver flakes (wt. %)	MWCNT (wt. %)	Epoxy (wt. %)	Hardener (gram)
5 (0.15g)	5 (0.15g)	90 (2.7g)	0.81
	6 (0.18g)	89 (2.67g)	0.801
	7 (0.21g)	88 (2.64g)	0.792

Figure 3.2: Carbon black ink, epoxy, hardener, silver flakes and MWCNT.

Figure 3.3: Levelling screw.

The amount of material used for the hybrid ECA formulation is as shows in Table 3.5. Here, the levelling screw as shown in Figure 3.3 is adjusted until the water level indicator is in the centre. The plastic container is then position at the centre of the Mettle Toledo balance machine and set to calibration every time materials is added. Then, the filler loading is placed into the container and grip it with an adapter shown in Figure 3.6 in the Thinky "ARE 310" centrifugal mixer machine and the Mettler Toledo balance is adjusted according to the gross weight measured by total gross weight of the filler loading, container and the adapter itself then run for 5 minutes with 2000 rpm spinning speed.

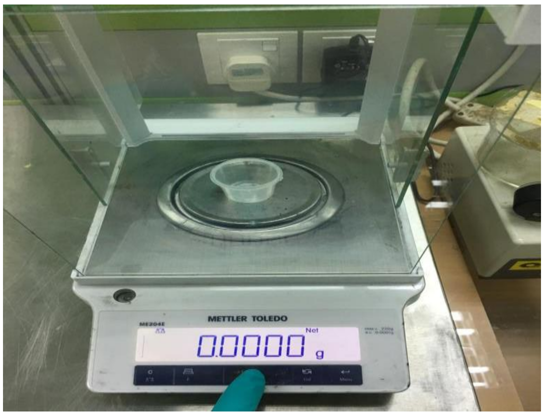


Figure 3.4: Mettler Toledo Balance machine.

Figure 3.5: Thinky “ARE 310” mixer machine.

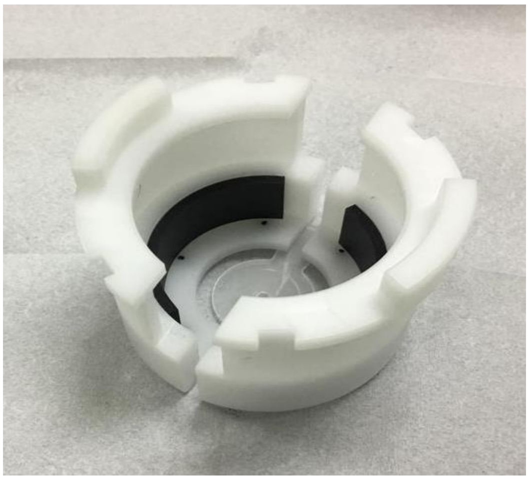


Figure 3.6: Adapter for the container.

Epoxy with specific amount pour into the plastic cup.

Hardener = 30% of epoxy weight (gram). +

Put silver flakes + MWCNT inside container.

+

Electrically conductive adhesive (ECA)

Spin for 5 minute

Fabricate for sheet resistance test

Pre- heat the oven (100°C) for 15 minutes.

Places the uncured ECA inside oven and heat up for ½ hour.

Cured ECA

Figure 3.7: The hybrid ECA preparation flow process.

For the formulation work, one plastic container is used for each specimen, to collect the right amount of materials as calculated and discussed earlier. The Mettler Toledo balance is reset to “zero” each time a new materials is added for the blend, as shown in Figure 3.4. This step is repeated for all the different types of hybrid ECA formulated, containing MWCNT filler loading in the range 5wt.%, 6wt.%, 7wt.% as shows in Figure 3.7. The hybrid ECA is the applied onto the substrate and put into the oven for 100°C for half an hour and let it cool down at air temperature. Figure 3.8 is shows blended hybrid ECA in container.

Figure 3.8: Mixed hybrid ECA in plastic container.

3.4 Fabrication of Printed hybrid ECA on Substrate

The substrate is cut using the laser cutter machine (Trotec® Speedy 〖300^{TM}〗 Flexx), as shown in Figure 3.9. The sample dimension of 88.9 mm x 114.3 mm is entered in the machine software, to achieve an accurate cutting piece of substrate sheet.

Figure 3.9: Laser cutter machine.

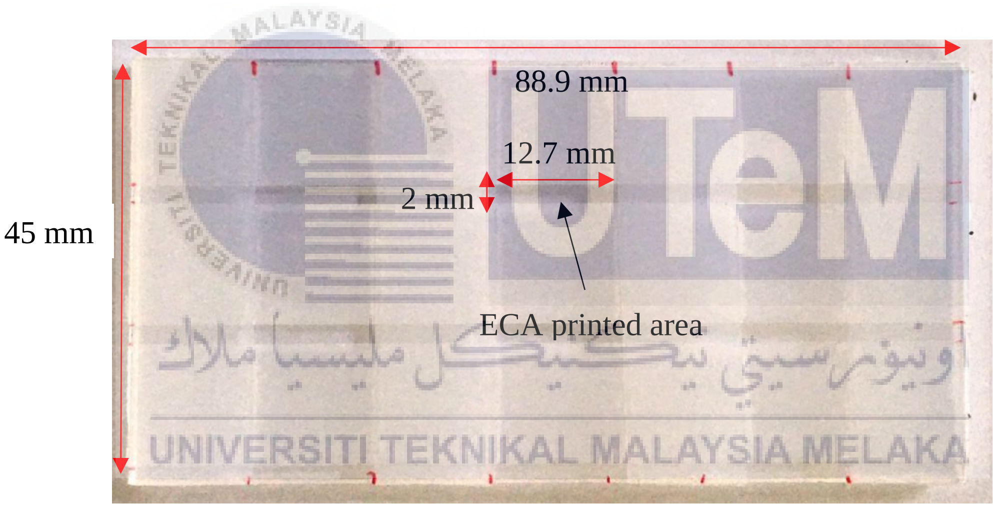


Figure 3.10: Substrate sheet.

Once the substrate sheet is prepared, a 3M scotch tape is used to create the template for printing hybrid ECA onto the substrate, and this step is repeated twice to achieve the desired nominal hybrid ECA thickness, as shown in Figure 3.10. Here, the uncured hybrid ECA is applied onto the substrate sheet all over the dedicated print area, squeeze and flatten by razor blade, as shown in Figure 3.11. The oven is pre-heat 100°C for 15 minutes, the put the uncured ECA into the oven for 100°C for half an hour. The cured hybrid ECA is shows in Figure 3.10.

Figure 3.11: Printed hybrid ECA on substrate sheet.

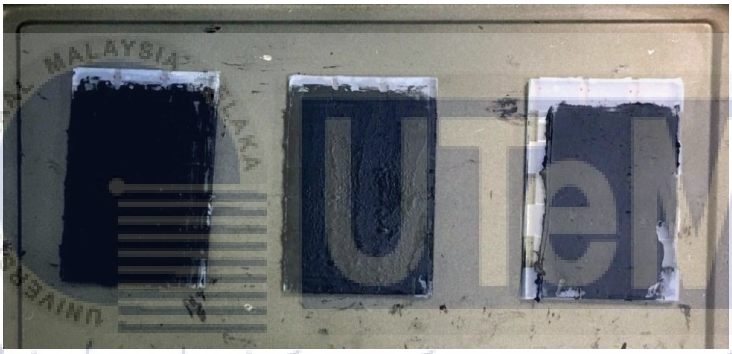


Figure 3.12: Cured hybrid ECA on substrate sheet.

The 3M scotch tape is tear off to form only the printed hybrid ECA area on the substrate sheet as shows in Figure 3.12, and use for the 4-point probe to measure their sheet resistance.

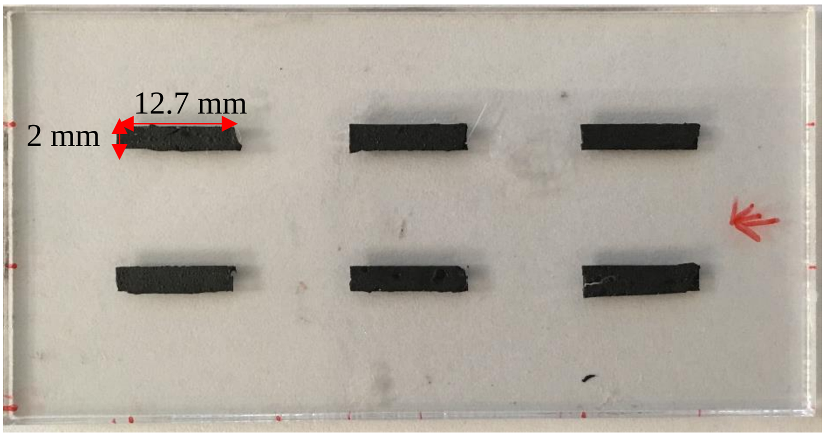


Figure 3.13: Printed hybrid ECA on substrate sheet.

3.5 Electrical Conductivity Test

A JANDEL model rm3000+ 4-point probe is used to measure the resistivity of printed hybrid ECA as shown in figure 3.15, by referring to the ASTM f390 as a standard guideline. One specimen contains 6 strips, and for every strip, a minimum of 3 readings in term of the resistivity is collected, as shows in Figure 3.13. The data collected form the 4-point probe is then imported into excel file to plot the results obtained from the experiment. Precaution is made during measurement, in which the 4-point probe memory is reset prior to testing, to avoid the data to be mixed up with other specimens.

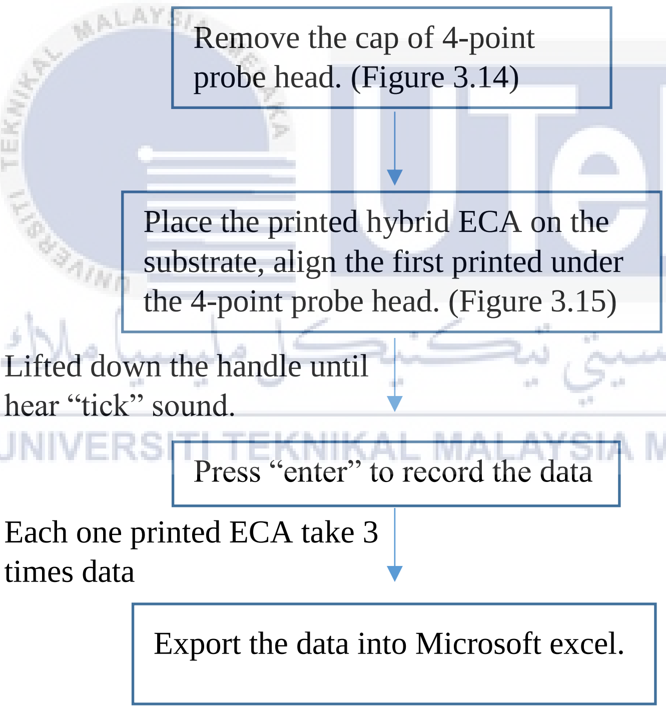


Figure 3.14: The flow process on how the resistivity data is measured and collected for analysis using the Microsoft software.

Figure 3.15: JANDEL model rm3000+ 4 point probe.

Form all the experiment recorded and imported in Microsoft excel, the sheet resistance calculation formula is expressed in equation (3.4) as follow:

$$R_s = G\,\frac{V}{I} \tag{3.4}$$

Whereby R_s is sheet resistance, $\frac{\Omega}{sq}$;

G is correction factor; 1.9475;

V is voltage; and

I is current.

The volume resistivity is calculated by using equation (3.5) as follow

$$P = \frac{V}{I}\,Gt,\ \Omega.\text{cm} \tag{3.5}$$

Whereby t is the thickness of printed ECA sample (cm)

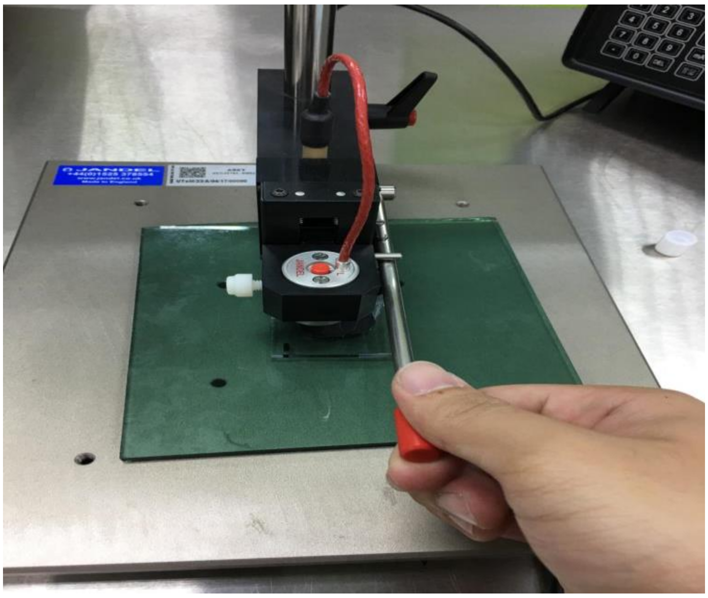


Figure 3.16: Demonstration of measuring resistivity using the 4-point probe.

3.6 Mechanical Properties

3.6.1 Lap Shear Test

For the mechanical performance test, the universal testing machine will be used for lap shear test. This is most common and widely used technique in determining the bonding and benchmarking the performance of their materials, ASTM D1002 (Trinidad et al., 2017).

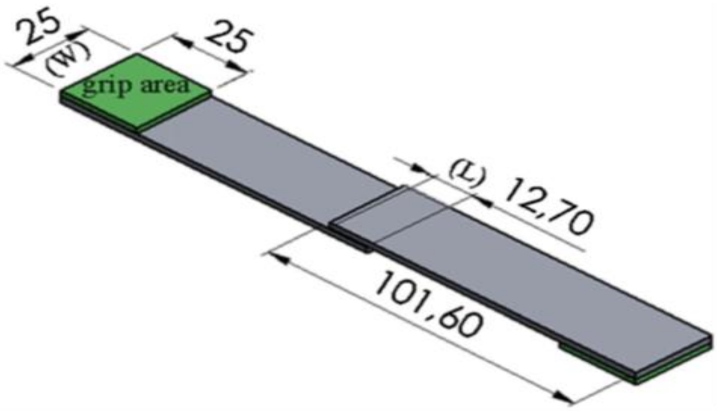


Figure 3.17: Schematic view of the tensile lap shear joint sample (Ekrem *et al.*, 2016).

The lap shear strength, τ (MPa) determined by using the Equation (3.6):

$$\tau = \frac{F}{A} \tag{3.6}$$

The lap shear strength is τ in MPa the F is load in newton (N) and area (A) is the cross-sectional in mm^2 (Baudot and Galy, 2014).

Figure 3.18: Universal Material Testing machine.

The Universal Material Testing machine use to performance lap shear test, there are 5 sample specimen will run the lap shear test for each filler loading. The flow process on preparing the specimen as shows in Figure 3.19. Firstly, specific amount of epoxy, silver flakes, MWCNT, and harder is poured into the container. The container is inserted inside adapter and measured in term of their gross weight, the balance is then adjusted according to total gross weight and the Thinky “ARE 310” mixer machine is then ready to be operated, which is set to standard mode, with a constant rotational speed of 2000 rpm for a total of 5 minute. The uncured hybrid ECA is then applied onto the aluminium substrate and a razor blade is used to squeeze and flatten the paste, as shows in Figure 3.20. During this stage, all the specimens need to place inside designed jig so that they can be properly cured accordingly inside the oven for 100°c for an half hour, as shows in Figure 3.19.

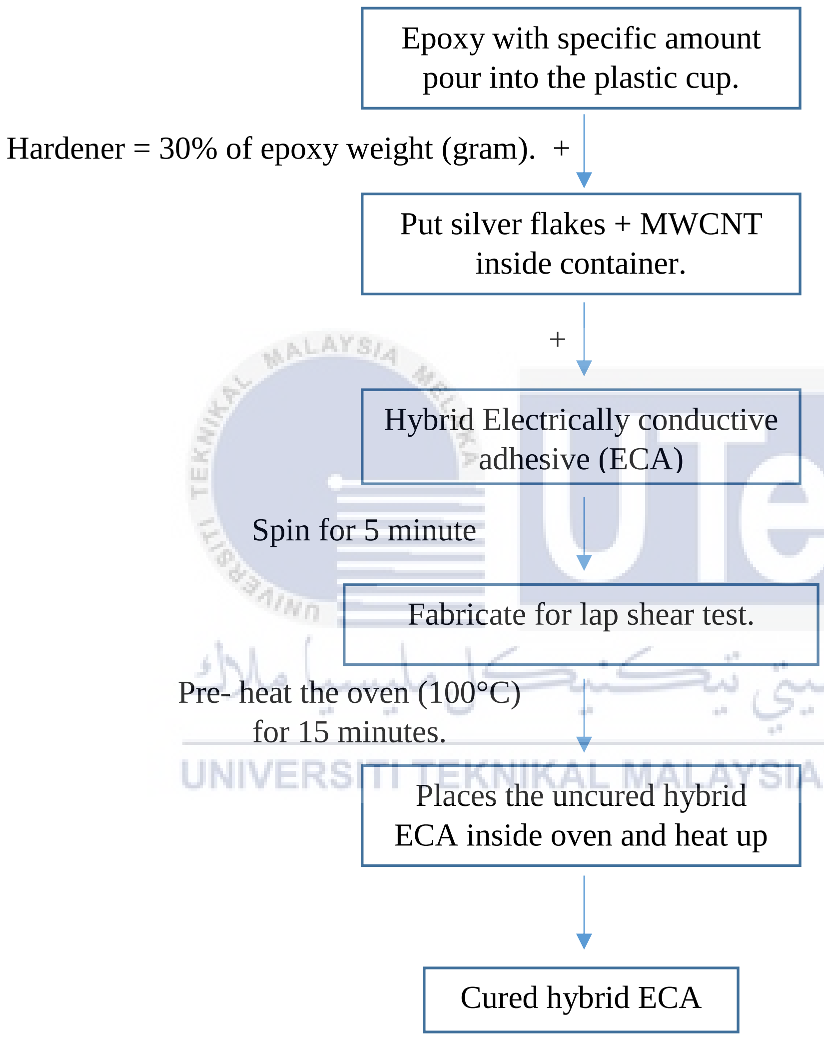


Figure 3.19: The fabrication lap shear test flow process.

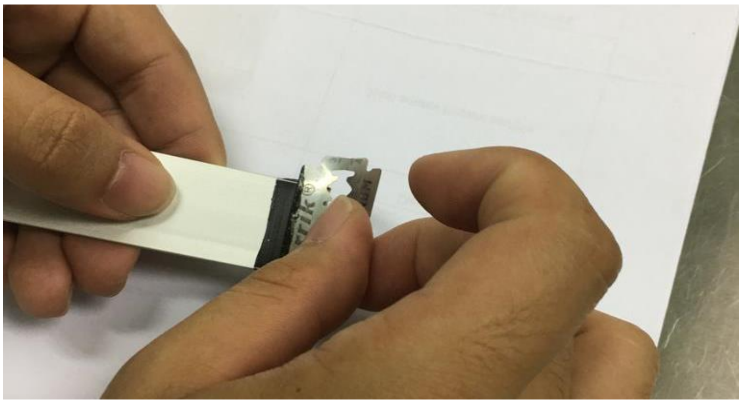


Figure 3.20: Printed hybrid ECA on aluminium substrate.

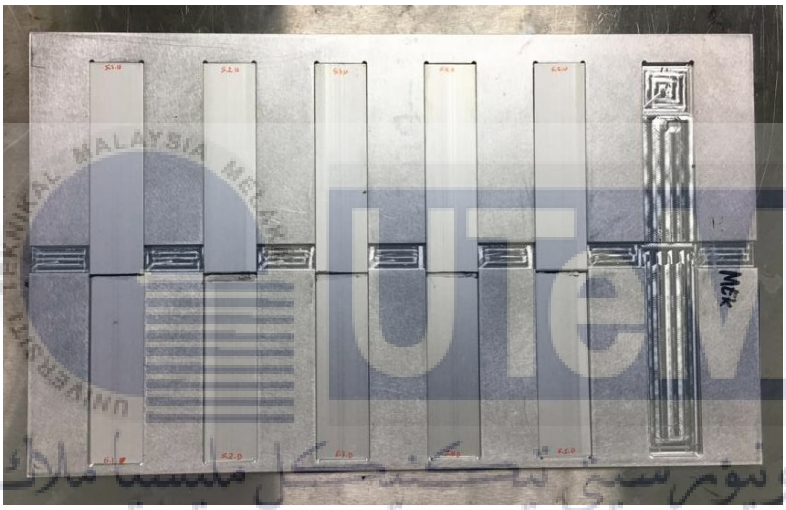


Figure 3.21: Cured hybrid ECA ready for lap shear test.

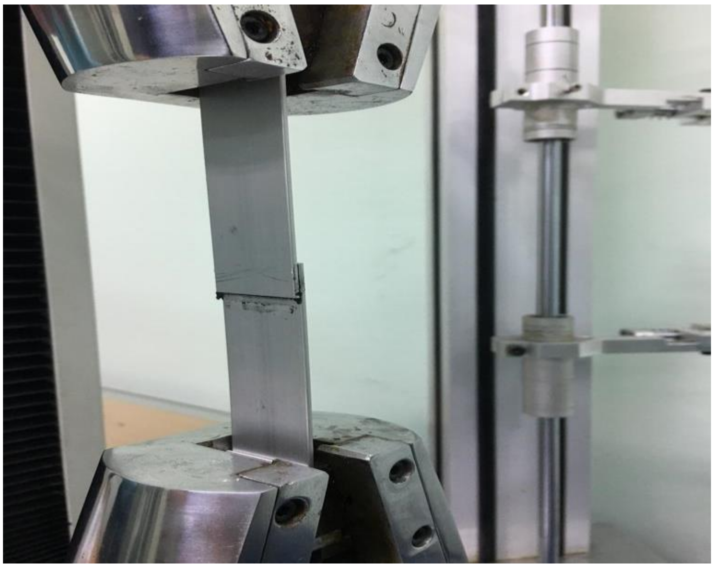


Figure 3.22: Lap shear testing test set up using a Universal Testing Machine, UTM.

Tighten specimen on UTM machine. (Figure 3.20)

↓

Run 2101(C) software. (Figure 3.23)

Tighten the specimen with turning wrenches. ↓

Press “run” to begin the test.

Each filler loading run 5 times test with 5 pieces specimen. ↓

Export the result into Microsoft excel.

Figure 3.23: The flow process on how the lap shear test result is conducted and collected for analysis using the Microsoft software.

Figure 3.24: Glues the specimen with 25mm x 25mm aluminium square pieces.

To ensure that all the specimen is aligned with the gripping system of the UTM machine, good gripping is required, that is by introduction end-tab on the samples, whereby each end is glued with an ECA aluminium substrate, as shows in Figure 3.24.

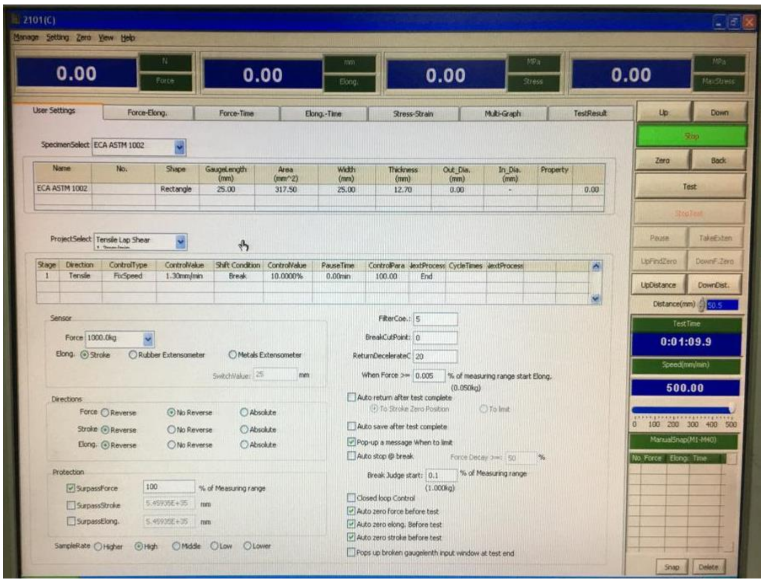


Figure 3.25: 2101 software for Lap Shear Test.

3.6.2 Analysis on Failure Mode

The following lap shear testing, each sample is inspected visually to observe the type of failure mode of the adhesive with different filler loading of the MWCNT. The observation is reported in Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the results following the experiment work on the electrical and mechanical characterization of the hybrid ECA with MWCNT (filler loading between 5 to 7 wt.%) and combined with silver flakes (5 wt.%) as second conductive filler for the hybrid ECA system is presented and discussed.

4.2 Electrical Performance of Hybrid Electrically Conductive Adhesive (ECA) With Varying Filler Loading.

The performance of hybrid ECA with varying MWCNT and silver flakes filler loading is present in terms of their sheet resistance by using JANDEL 4-point probe. As shown in Figure 4.1, the volume resistivity is calculated with reference to Equation. (3.4) (Zulkarnain, Mariatti and Azid, 2013). Here, is aimed that increasing filler loading contents will result in decreasing resistivity, so that enhanced conductivity is achieved when hybridizing the ECA using the two conductivity filler.

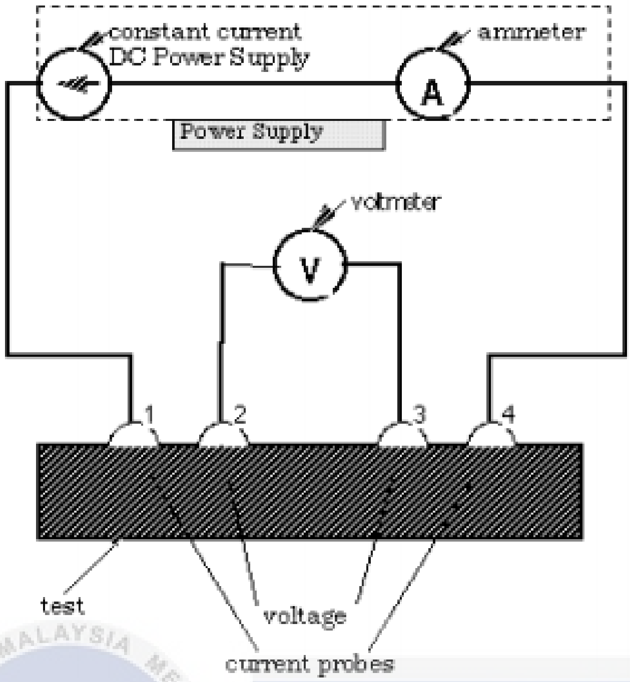


Figure 4.1: Schematic of 4-point probe (Vangala, 2010).

Based on Ohm's law the value of volume resistivity also defined as electrical resistance. It is anticipated that the resistivity of the composite will be decreasing slowly as filler content increase, and quickly decrease when the filler content over the critical volume (Vc). The adhesive conductive channels will starts forming 3-D network conductive loops, once the percolation threshold meet the requirement (Suriati, Mariatti and Azizan, 2011).

4.2.1 The Effect of Filler Loading on Multi-Walled Carbon Nano-Tubes Sheet Resistance and Volume Resistivity.

The measured sheet resistance of the hybrid ECA with varying MWCNT filler loading with JANEL 4-point probe to measure it sheet resistance with varying filler loading is shown in Table 4.1. Based on the experiment result shows in Figure 4.2, it is clear that average sheet resistance decrease from 3,233.17$\frac{\Omega}{sqr}$ for 5 wt.% filler loading to 2,314.06$\frac{\Omega}{sqr}$ for 6 wt.% filler loading and lastly drop at 1,109.45$\frac{\Omega}{sqr}$ when filler loading is reaching 7 wt.%. such observation is in good agreement with an earlier finding by Yuen *et al.*, (2007). The percolation threshold reached at 6 wt.% and 7 wt.% created conductive path in decreasing hybrid ECA resistivity and increasing conductivity (Patole and Lubineau, 2014). The trend suggest that an increase in filler loading will cause a decrease of the volume resistivity, as argued by Mantena (2009).

Table 4.1: Data of average sheet resistance and volume resistivity with varying filler loading.

Filler loading, wt.%	Average sheet resistance, $\frac{\Omega}{sqr}$	Average volume resistivity, Ω.cm
5	3233.17 ± 243.06	20.21 ± 1.52
6	2314.06± 962.34	14.46 ± 6.01
7	1109.45 ± 1333.95	6.93 ± 8.34

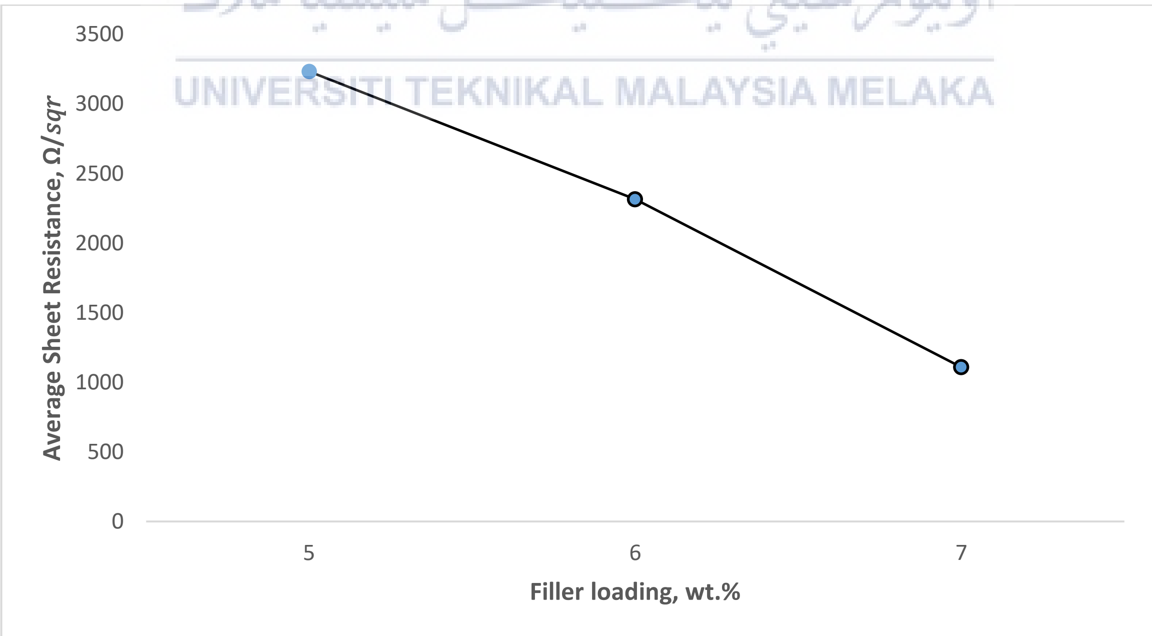


Figure 4.2: Graph of average sheet resistance, Ω /sqr against MWNCT filler loading (wt.%).

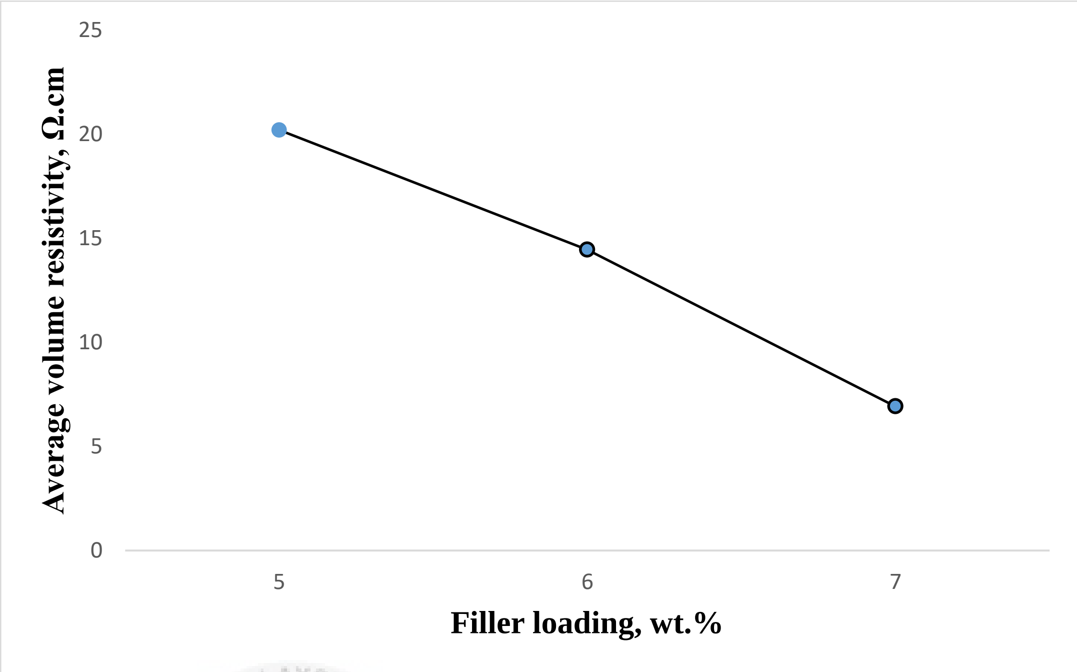


Figure 4.3: Graph of average volume resistivity, Ω.cm against MWCNT filler loading, (wt.%).

From Figure 4.3, increasing filler loading from 5 wt.% to 7 wt.% the average volume resistivity of hybrid ECA decreases, as shown in Figure 4.2. A higher volume resistivity is observed with 5 wt.% of filler loading, with a value of 20.21 Ω.cm. The average volume resistivity slowly drops down below a magnitude of 10 Ω.cm when the filler loading is added up to 7 wt.%. Further increase of filler loading leads to a too viscous hybrid ECA, which appear to affect the volume resistivity, therefore resulting in an enhance electrical conductivity (Vangala, 2010).

Moreover, based on the comparison of the average of resistance in Table 4.2, it was observed that, as hypothesized earlier in this chapter, the hybrid ECA exhibit better electrical conductivity as compared to those of the normal ECA reported in the literature using epoxy with MWCNT of similar filler loading. The hybrid ECA sheet resistivity decrease when the with increasing amount of filler loading (Mirmohammadi, Sadjadi and Bahri-Laleh, 2018).

Clearly, there is an enhancement between 30 to more than 80% relative to the normal ECA system (Figure 4.4), which suggest a dramatic improvement in conductivity when a 5 wt.% of silver flakes are added to the ECA composite system.

Table 4.2: Comparison of average sheet resistance between hybrid ECA and normal ECA with varying filler loading (Raheem, 2018).

Filler loading, (wt.%)	Average sheet resistance, (K Ω /sqr.)		Electrical conductivity enhancement from hybridization.
	Hybrid ECA	Normal ECA	
5	3.23 ± 243.06	10.66±3.19	30.30%
6	2.31 ± 962.34	3.79±1.89	60.95%
7	1.11 ± 1333.95	1.36±0.49	81.62%

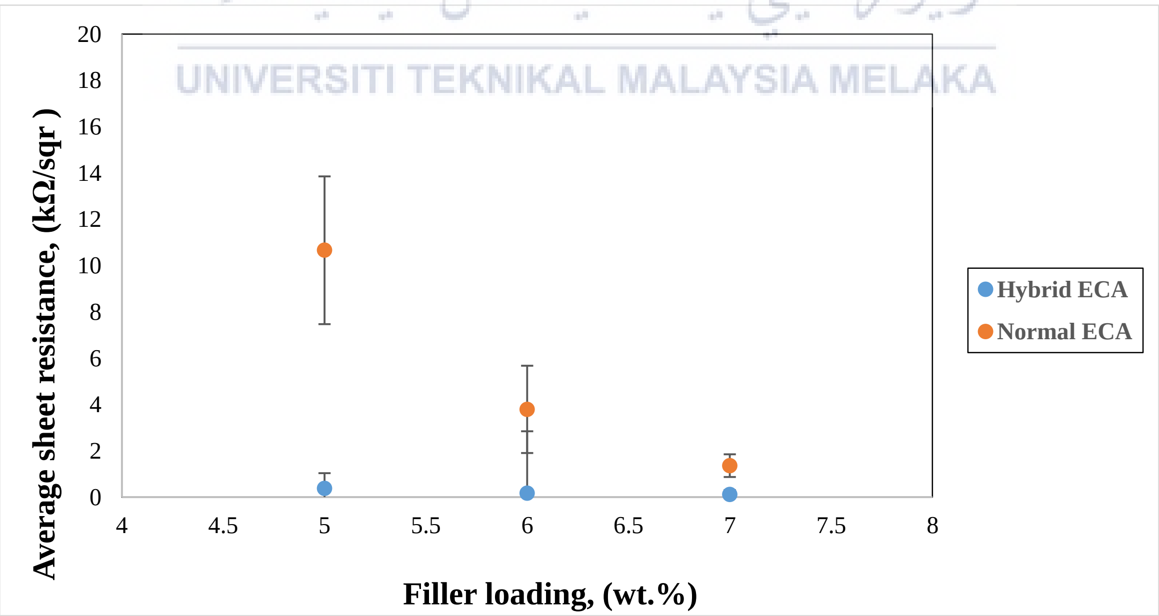


Figure 4.4: Average sheet resistance vs MWCNT filler loading wt.% of hybrid ECA in comparison with normal ECA (Raheem, 2018).

4.3 Mechanical Performance of Hybrid Electrically Conductive Adhesive (ECA) With Varying Filler Loading.

4.3.1 The Effect of Filler Loading on the Lap Shear Strength of Hybrid Electrically Conductive Adhesive (ECA).

The lap shear test is conducted using 2101 (C) software and the lap shear strength data is collected as shows in Table 4.3.

Table 4.3: Data of average lap shear strength with varying filler loading.

Filler loading, wt.%	Average lap shear strength, τ (MPa)	Standard derivation
5	8.61	1.21
6	7.49	1.05
7	7.03	1.96

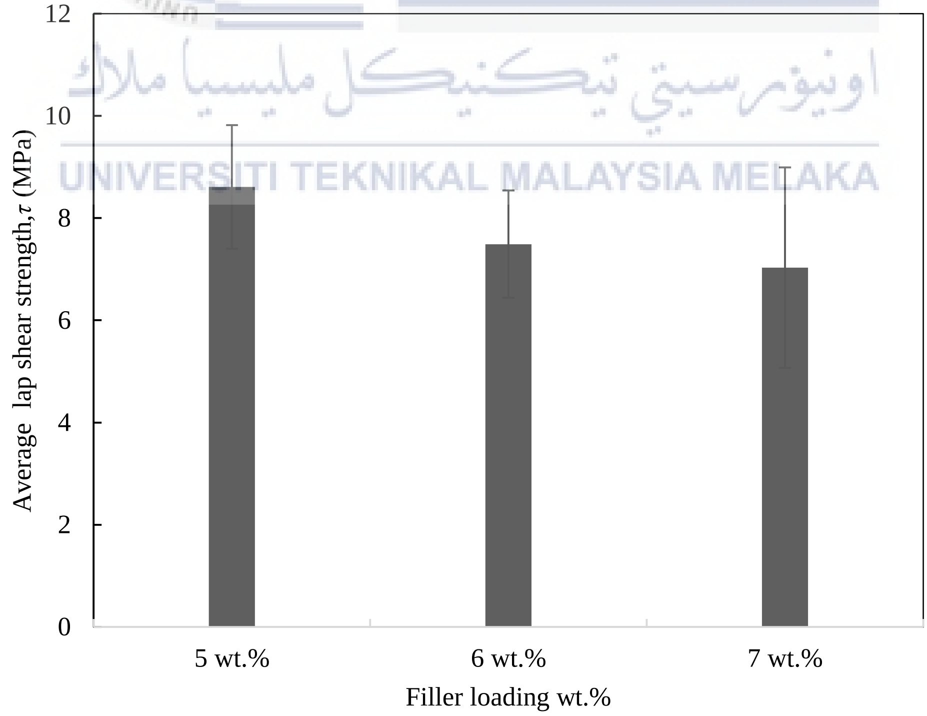


Figure 4.5: Average lap shear strength, τ (MPa) against MWCNT filler loading (wt.%).

From the Figure 4.5, it is observed that the ECA average lap shear strength, τ is higher at 5 wt.% of MWCNT and the trend shows that the property decrease with increasing MWCNT filler loading, as reported by earlier work by Mantena (2009). The shear strength of hybrid ECA adhesive is obtained with a value of 8.61 MPa with MWCNT filler loading of 5 wt.%. With increasing filler loading, at 6 wt.% MWCNT the shear strength reached a magnitude of 7.49 MPa, in which amount of epoxy is reduced by 1 wt.% relative to the total amount of composite volume, thereby causing the hybrid ECA shear strength to drop below 8 MPa. Such observation continue until the MWCNT filler loading is added up to 7 wt.%.

Table 4.4: Comparison of average lap shear strength between hybrid ECA and normal ECA with varying filler loading (Raheem, 2018).

Filler loading, wt.%	Average of lap shear strength, τ (MPa)	
	Hybrid ECA- Epoxy + MWCNT + silver flakes	Normal ECA – Epoxy +MWCNT (Raheem, 2018).
5	8.61± 1.21	8.58 ± 1.55
6	7.79 ± 1.05	7.67 ± 1.20
7	7.03 ± 1.96	5.85 ± 2.03

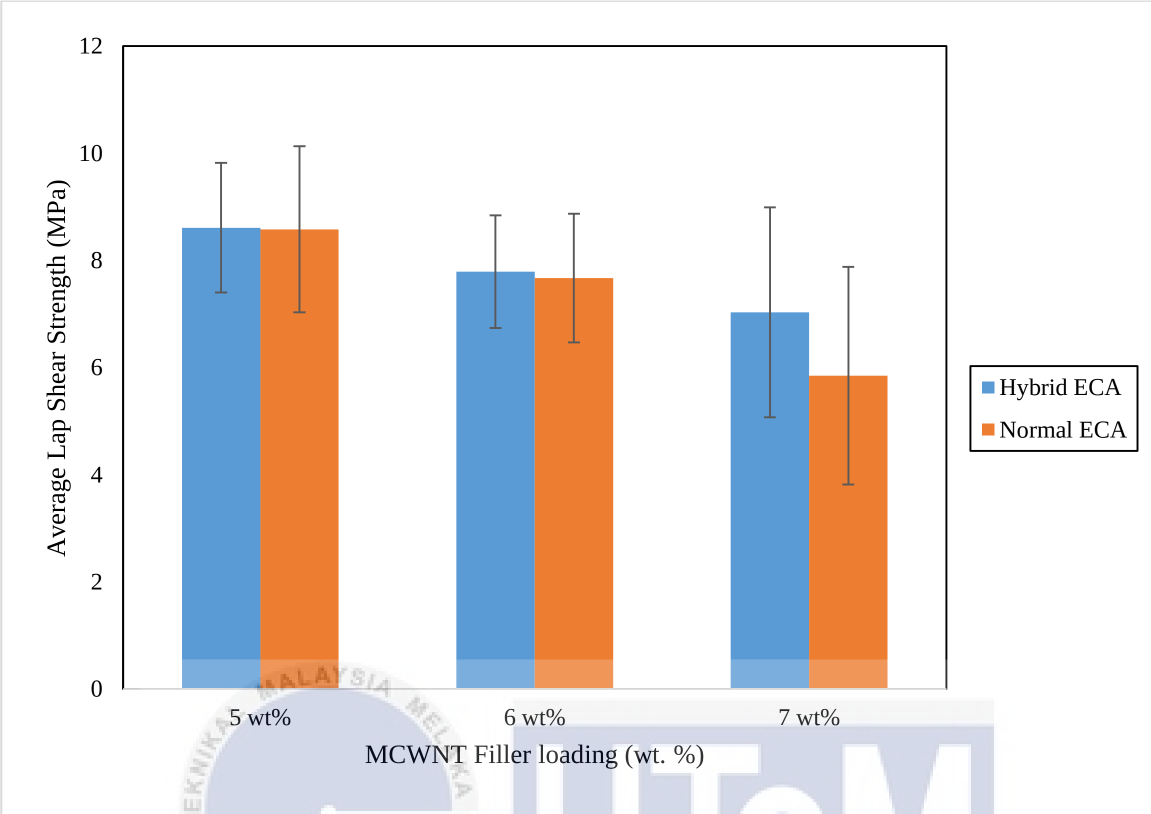
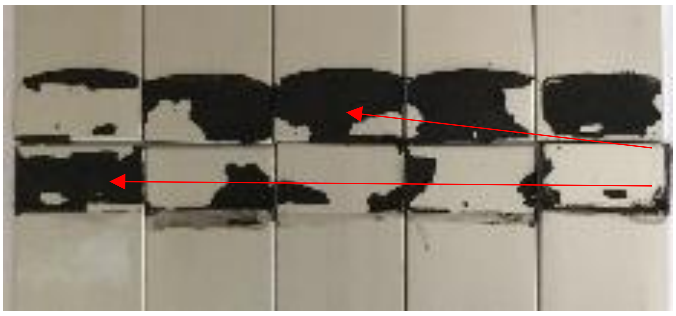


Figure 4.6: Comparison of average lap shear strength between hybrid ECA and normal ECA with varying filler loading (Raheem, 2018).

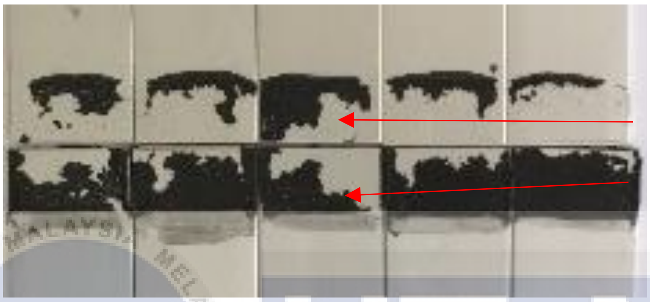
Correlation between the average lap shear strength of the hybrid ECA in comparison to those of the normal ECA as published in the literature by Raheem, 2018 is given in Figure 4.6. The hybrid ECA apparently has higher strength compared to normal ECA. However, with increasing filler lap shear strength, which is in good agreement with the literature (Li and Xiang, 2018).

Figure 4.7, 4.8, and 4.9 show the hybrid ECA specimen surface with varying filler loading following lap shear testing (test mode). Hybrid ECA with 5 and 6 wt.% filler loading exhibit the cohesive adhesive failure, since the adhesive is retained on both sides of the substrate. However, a different failure mode is observed at higher MWCNT filler loading, i.e., at 7 wt.%, in which the hybrid ECA exhibit an adhesive failure, which is an indication of an inferior type of adhesive failure, with the adhesive retained only on one side of the (Ayatollahi *et al.*, 2011).



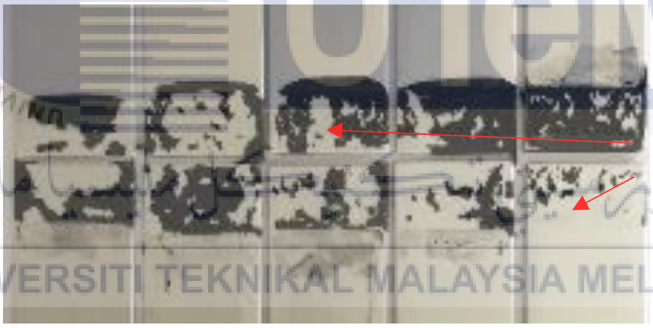
Cohesive +
adhesive failure
ECA retained at
both side.

Figure 4.7: 5 wt% of hybrid ECA mechanical test specimen.



Cohesive +
adhesive failure
ECA retained at
both side.

Figure 4.8: 6 wt% of hybrid ECA mechanical test specimen.



Adhesive failure
ECA retained
mostly on one side.

Figure 4.9: 7 wt% of hybrid ECA mechanical test specimen.

CHAPTER 5

CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

5.1 Conclusion

From the experiment results obtained in this research, two conclusions are drawn based on the two objectives.

From the volume resistivity of cured hybrid ECA, there is a reduction in the resistivity with increasing filler loading, from 5 to 7 wt.% of the MWCNT added to the 5 wt.% Ag in the hybrid ECA system. In addition, the percolation threshold is observed at 7 wt.% of the MWCNT filler loading, similar to the case of normal ECA. In which the resistivity dropped once reaching the percolation point and there no practical connection with filler loading before percolation exist.

Moreover, there is a dramatic improvement when hybridizing the ECA with a combination of silver and MWCNT when correlated with similar adhesive using purely MWCNT of similar filler loading.

In terms of the mechanical performance via lap shear test, the hybrid ECA has highest lap shear strength which is 8.61 MPa at 5 wt.% filler loading. With increasing filler loading up to 7 wt.%, the average lap shear strength reduced to less than 7.03 MPa, suggesting that increasing of filler loading does not aid further in improving the lap shear strength. Moreover, in comparison with normal ECA with similar MWCNT filler loading, it is apparent that the lap shear strength of the hybrid ECA is superior to those of the normal ECA. With two type of adhesive failure; that is (i) the cohesive-adhesive failure-stronger and (ii) adhesive failure, that is for the case of hybrid ECA with 7 wt.% of the MWCNT.

5.2 Recommendation for future works

As extension of the works which may be appropriate in studying the performance of the hybrid ECA may consider the following:

- Different route of mixing using centrifugal mixer: using standard mode and additional step of “defoam” as included in the new Thinky Mixer Model to evaluate the effect of degassing on the electrical conductivity of the hybrid ECA and correlate with normal ECA.
- The effect of hydrothermal aging on the functional properties of the hybrid ECA: subject the samples to various temperature and moisture in an environmental chamber for a specific period to mimic an actual service operation condition of the hybrid ECA and correlate with normal ECA.
- To evaluate the wetting behaviour of the hybrid ECA using contact angle tool to understand the correlation between the use of different substrate and surface condition on the performance of the hybrid ECA and correlation with normal ECA.

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